OFFICE OF NAVAL RESEARCH

Contract N00014-87-C-0713

Technical Report No. 7

Boron-Nitride Preceramic Polymer Studies

by

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To be Published

in

Proceedings of the 12th Annual Conference on
Composites and Advanced Ceramics

January 17-20, 1988
Cocoa Beach, Florida

Ultrasystems Defense and Space Inc.
16775 Von Karman Avenue
Irvine, California 92714

February 22, 1988

Unclassified
SECURITY CLASSIFICATION OF THIS PAGE

ADA197359

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1a. REPORT SECURITY CLASSIFICATION Unclassified	1b. RESTRICTIVE MARKINGS
2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release Distribution unlimited
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE	
4. PERFORMING ORGANIZATION REPORT NUMBER(S) Technical Report No. 7	5. MONITORING ORGANIZATION REPORT NUMBER(S)
6a. NAME OF PERFORMING ORGANIZATION Ultrasystems Defense and Space Inc. 6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION Department of the Navy
6c. ADDRESS (City, State, and ZIP Code) 16775 Von Karman Avenue Irvine, CA 92714	7b. ADDRESS (City, State, and ZIP Code) Arlington, VA 22217
8a. NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research 8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-87-C-0713
8c. ADDRESS (City, State, and ZIP Code) Code 1113 800 North Quincy Street Arlington, VA 22217	10. SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO. / PROJECT NO. / TASK NO. / WORK UNIT ACCESSION NO.

11. TITLE (Include Security Classification)

Boron Nitride Preceramic Polymer Studies

12. PERSONAL AUTHOR(S)
K. J. L. Paciorek and R. H. Kratzer

13a. TYPE OF REPORT	13b. TIME COVERED FROM ____ TO ____	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT

16. SUPPLEMENTARY NOTATION

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Boron nitride fibers and boron nitride coatings on alumina fibers are described. The boron nitride fibers were obtained from fusible preceramic polymer. For the coatings, a non-fusible, organic solvent soluble, preceramic polymer was utilized. Transformation of the preceramic polymers to boron nitride ceramic was accomplished in an ammonia atmosphere. The fully cured ceramics are colorless and do not undergo weight or shape changes when heated to 1000°C in nitrogen or air.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT ☐ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS	21. ABSTRACT SECURITY CLASSIFICATION Unclassified
22a. NAME OF RESPONSIBLE INDIVIDUAL Kenneth J. Wynne	22b. TELEPHONE (Include Area Code) (202) 696-4410 22c. OFFICE SYMBOL

DD Form 1473, JUN 86 *Previous editions are obsolete.*

SECURITY CLASSIFICATION OF THIS PAGE
Unclassified

BORON NITRIDE PRECERAMIC POLYMER STUDIES

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Paper presented at the 12th Annual Conference on Composites and Advanced Ceramics, Cocoa Beach, FL, January 17-20, 1988.

Two boron nitride preceramic polymers were developed: a fusible soluble composition amenable to fiber spinning and an infusible organic solvent soluble material suitable for preparation of BN coatings, laminating resins and boron nitride densification. On thermal curing of the preceramic polymers in reactive or inert atmospheres, no boron containing compositions are volatilized indicating a theoretical yield of ceramic. The fully cured materials are colorless and do not undergo weight or shape changes when heated to 1000°C in nitrogen or air. Synthesis of the preceramic polymers, their transformation into boron nitride ceramics, and end item production will be discussed.

Introduction

Pure boron nitride exhibits a number of unique properties. It is optically transparent over large regions of the electromagnetic spectrum, it is a dielectric remaining non-conducting up to its melting point, it is lightweight with a density of 2.2, it is resistant to oxidation to at least 1000°C, has a high heat of

vaporization, and exhibits solid lubrication characteristics. Boron nitride, furthermore, has a low thermal expansion coefficient matching that of graphite and it is chemically inert towards many oxide ceramics at their melting points making it an ideal interphase material for, e.g. a Al_2O_3 fiber/SiO_2 matrix composite. Finally, boron nitride fibers are expected to possess a high Young modulus coupled with high strength[1].

Compared with carbon fiber and carbon/carbon technology in general, boron nitride production and especially processing knowledge is in its infancy. Boron nitride can be prepared via several routes in form of fine powder, which can be hot-pressed and sintered. This approach, however, does not lend itself to fiber or coatings applications. Boron nitride fibers have been prepared by nitriding boron oxide fibers, but nitridation invariably was incomplete and the presence of unconverted boron oxide rendered fibers of low strength and poor high temperature performance due to the low melting point of boron oxide. However, a 1976 Japanese patent[2] claimed the preparation of BN fibers with respectable tensile strength which were produced by controlled pyrolysis of N-phenyl-B-amino borazine via a processible preceramic polymer. Unfortunately, the results of this work could not be reproduced[3] primarily because of carbon retention. Only recently have preceramic BN based polymers become available which can be transformed via chemical and/or thermal processes into pure boron nitride or, as a minimum, into compositions free of carbon

and oxygen. In 1986, a BN preceramic polymer was described[4] which is fusible and soluble, can be melt spun into fibers, which in turn can be transformed into colorless BN fibers stable to at least 1000°C in air. Finally, in 1987, the syntheses of two novel soluble polymeric BN precursors were reported, one amenable to fiber coating applications[5], the other suitable for boron nitride preparation via sol-gel processing techniques[6].

Obviously, the application of a boron nitride coating on a substrate or the production of a boron nitride fiber are considerably more complex than the spinning of a Nylon fiber. As a ceramic, boron nitride is infusible, insoluble, and in general intractable. Accordingly, to make the preceramic BN precursor processible into desired shapes, this precursor must contain intramolecular components and substituents, which provide for processibility and inherent plasticizer action, but which are also capable of complete vaporization during transformation of the shaped preceramic into boron nitride. As far as is known at present, the amount of plasticizing substituents required to make the BN precursor processible is of the order of 65-75% by weight of the preceramic polymer, which translates into a possible yield of pure boron nitride of 25-35%. The mechanism of this transformation of preceramic polymer into the dense ceramic is, as in almost all other cases[7], only poorly, if at all, understood. However, the fact that apparently void-free BN fibers can be produced and that well adhering continuous coatings of BN on

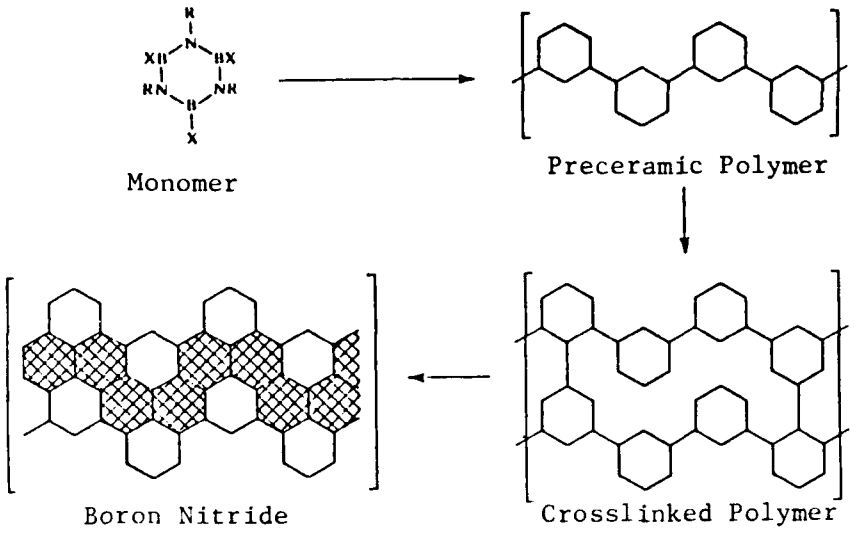
several substrates can be reproducibly obtained shows that a detailed understanding of the underlying mechanisms is not a prerequisite for final product formation.

Experimental

Due to the oxygen and, in particular, moisture sensitivity of most of the starting materials and intermediates, all operations were performed using nitrogen by-pass, inert atmosphere chambers, or high vacuum techniques. Only after final curing at 970-1000°C was the product exposed to the laboratory atmosphere. Fibers were either drawn by hand from the polymer heated to 110-120°C or spun from the melt by Dow Corning. Coatings were applied by dipping the substrate into an ~6-14% by weight solution of the preceramic polymer in pentane or hexane followed by evaporation of the solvent. Transformation into boron nitride of fibers or coatings was achieved by gradual heating from 50°C to 1000°C in an ammonia atmosphere. Photomicrographs were obtained using standard SEM techniques.

Results and Discussion

The general idea of producing boron nitride from monomeric borazines via a processible preceramic polymer can, in an over-simplified manner, be represented by the following scheme:

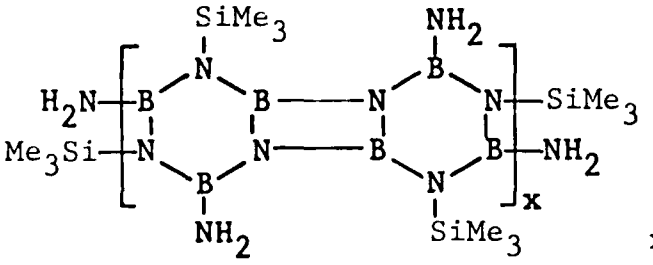


This scheme consists of producing linearly connected chains of borazine rings by elimination of the B and N substituents from the borazine monomer as a volatile compound RX, followed by more severe thermal treatment to create bonds between adjacent chains of rings via further elimination of the RX moieties with a final production of the boron nitride network. Following this general approach, two basic types of preceramic polymers were produced. The starting material for the first preceramic fusible and soluble polymer system was obtained by the reaction sequence:

$$BCl_3 \cdot TEA \xrightarrow{(96\%)} (Me_3Si)_2NBCl_2 \xrightarrow{(70\%)} [Me_3SiNBCl]_3 \xrightarrow[-78°C]{NH_3} [Me_3Si\text{-}NB\text{-}NH_2]_3 \quad (20\%),\ (100\%)$$

B-trichloro-N-tris(trimethylsilyl)borazine was reported previously[8] and its transformation to the amino derivative proceeded readily in an essentially quantitative yield[4,9]. The monomer thus obtained

was admixed with a singly bridged dimer. Further controlled pyrolysis at 200°C gave a mixture of doubly-bridged tetramers and octamers depicted below:

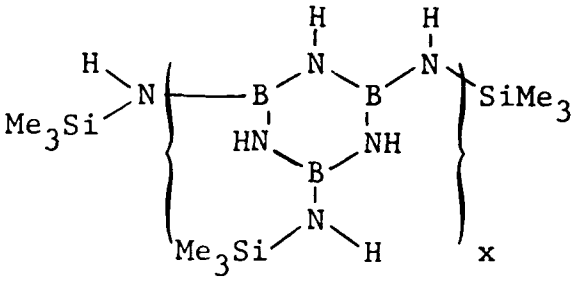


x = 2 and 4

The infrared spectrum of this preceramic polymer is given in Figure 1. This material was amenable to melt spinning and gave 11-20 μ diameter monofilament, shown in Figure 2a. Its cross-section is presented in Figure 3a. The "green" fibers were successfully cured to boron nitride ceramic fibers on gradual heating over 98 hr from 50-1000°C in an ammonia atmosphere. These cured fibers are depicted in Figures 2b and 3b. The absence of voids is apparent from Figure 3b. Inasmuch as the fiber shrinkage observed was minimal, it is believed that microporosity must be present. Post cure under tension at ∿1200°C should impart crystallinity and further densification, as well as increased strength. The infrared spectrum of the ceramic in film form derived from the same preceramic polymer from which the fibers were drawn is given in Figure 4. It shows clearly absence of absorptions other than those of boron nitride itself.

The second polymer system, which is not fusible but very soluble in pentane or hexane, was obtained by controlled

interaction of chloroborazine with hexamethyldisilazane. To obtain the soluble, preceramic polymer of the general form shown below, with x averaging 5,



required nonpolar solvents and rigid temperature control[5]. Using polar solvents, others[6] obtained crosslinked gel-like materials essentially free of silicon. The presence of the trimethylsilyl groups renders the material very soluble in organic solvents, 72 g/100 cc in hexane. Utilization of oxide fibers in an oxide matrix is very temperature limited, as mentioned earlier, due to eutectic formation. Thus, the true potential of the system cannot be reached. By introduction of a "non reactive" interphase such as boron nitride, these limitations can be overcome. The high solubility of the "pentamer", in conjunction with its infusibility, makes it thus an ideal coating candidate for oxide fibers such as alumina fibers. Due to its infusibility, there is no need to exercise caution during the curing process, inasmuch as there is no danger of material loss due to melting. It is evident from Figures 5b and 6b that well-adhering boron nitride coatings were achieved. The coating process was applied to Alumina FP fiber bundles (tows), yet no fusing of fibers was observed. The

cross-section view of the coated fiber (Figure 7b) clearly shows that a continuous coating was obtained. To assess whether pure boron nitride is indeed produced from the preceramic polymer, the transformation in an ammonia atmosphere was carried out on the bulk material in order to obtain a mass balance. The weight loss corresponded to the assigned preceramic polymer arrangement. Thermogravimetric analysis of the cured product revealed that no weight loss occurred in air up to 1000°C. The powder recovered after this treatment was unchanged in appearance as compared to the starting material.

Summary and Conclusions

The feasibility of preparing boron nitride preceramic polymers which are fusible and/or soluble and which can be transrormed via chemical and thermal processes into carbon free boron nitride has been demonstrated. Using the preceramic polymer approach and employing a relatively low melting preceramic polymer, fibers were spun in form of monofilaments and transformed into 8-10μ diameter colorless boron nitride fibers. Heating these fibers in air at 1000°C neither changed their weight nor their shape. Scanning electron microscopy (SEM) revealed the fiber surfaces, as well as fracture cross-sections to be apprently dense and void free. Employing pentane solutions of an infusible type of preceramic polymer, Alumina FP fiber tows were coated with boron nitride by dipping, solvent evaporation, followed by a cure

in an ammonia atmosphere and heating to 1000°C. SEM showed these coatings to be 0.2-0.5μ thick, continuous, and well-adhering without causing fusion or bonding between the individual fibers in the tow.

To fully utilize the potential of this preceramic polymer technology, it will be necessary to scale up the synthesis to produce the fusible polymer in quantities sufficient for larger scale fiber production, which in turn will make it possible to determine whether or not these fibers can be woven or in which form the maximum benefit in matrix reinforcement can be achieved. The same applies to the preparation of the soluble, but infusible preceramic polymer to allow an assessment whether the presently available oxide fiber coating technology can be extended to the coating of alumina fiber based fabric, as well as to other ceramic fiber substrates.

Acknowledgements

The partial support of this work by CMR/SDI, the cooperation of Dow Corning and Dr. Paul Lu in the fiber spinning efforts, as well as the collaboration of Ford Aeronutronic and Dr. David Paquette with the alumina fiber coating studies are gratefully acknowledged. Also acknowledged are the contributions by Dr. David Harris, Dr. Wilfried Krone-Schmidt, Mr. Steven Masuda, and Ms. Lily Lim.

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CAPTIONS FOR FIGURES

Figure 1. Infrared Spectrum of Molten BN Precursor

Figure 2a. Uncured BN Precursor Fiber

Figure 2b. Cured BN Fiber

Figure 3a. Cross-section of BN Precursor Fiber

Figure 3b. Cross-section of Cured BN Fiber

Figure 4. Infrared Spectrum of Cured BN Thin Film

Figure 5a. Uncoated Alumina FP Fiber 5,000x

Figure 5b. BN Coated Alumina FP Fiber 5,000x

Figure 6a. Uncoated Alumina FP Fiber 10,000x

Figure 6b. BN Coated Alumina FP Fiber 10,000x

Figure 7a. Cross-section of Uncoated Alumina FP Fiber

Figure 7b. Cross-section of BN Coated Alumina FP Fiber

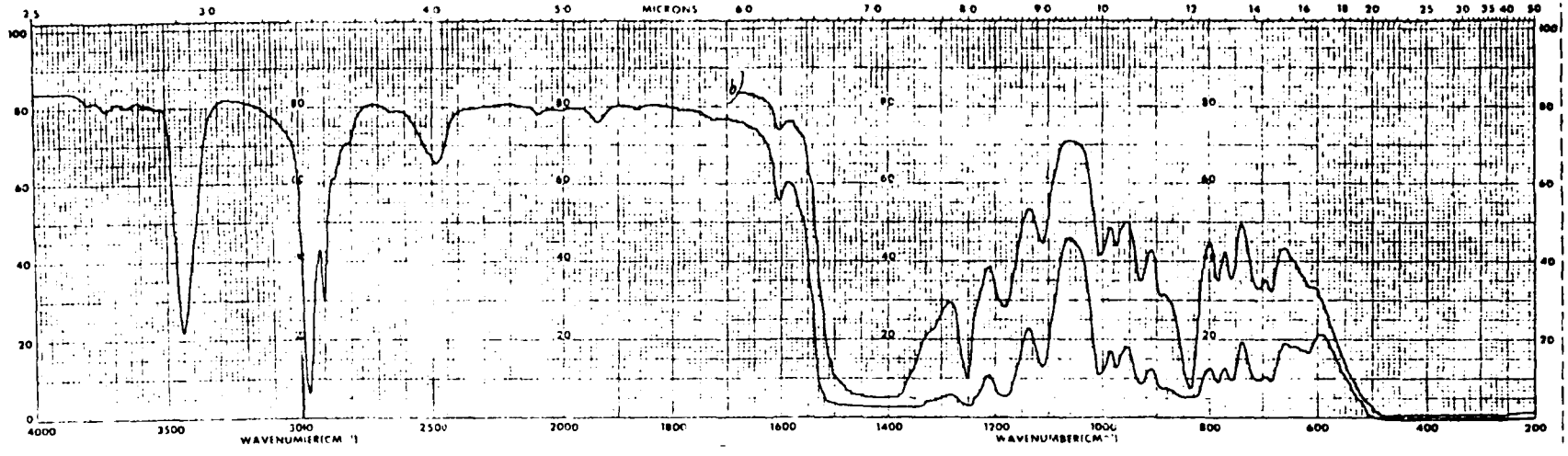

Figure 1

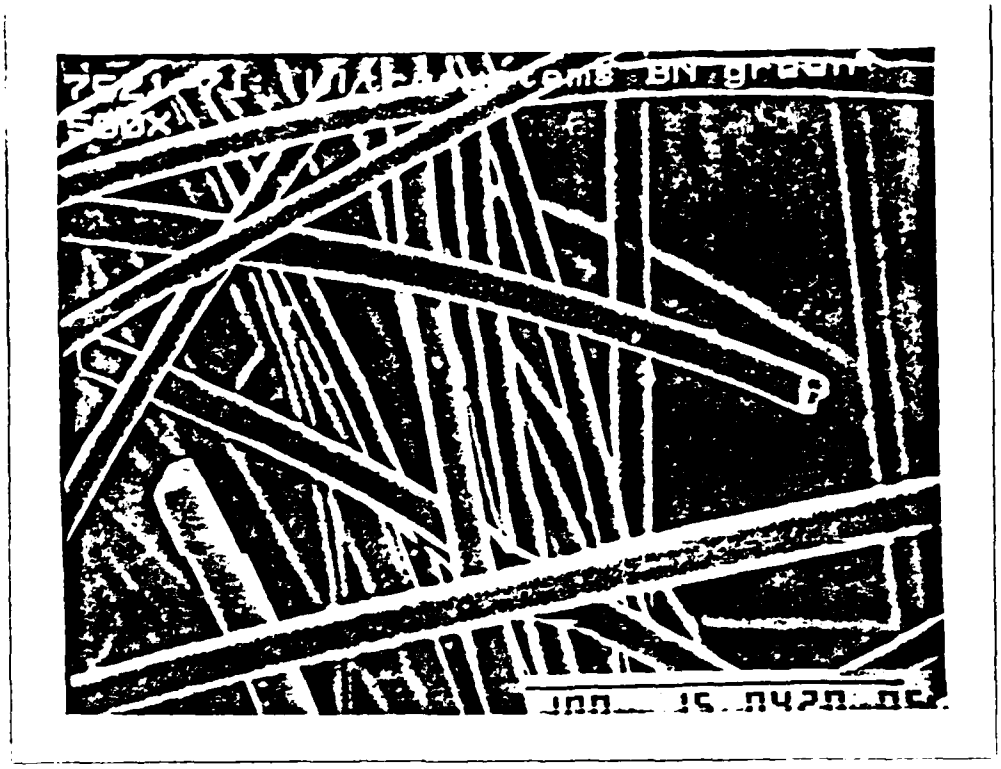

Fig. 2a UNCURED BN PRECURSOR FIBER

Fig. 2b CURED BN FIBER

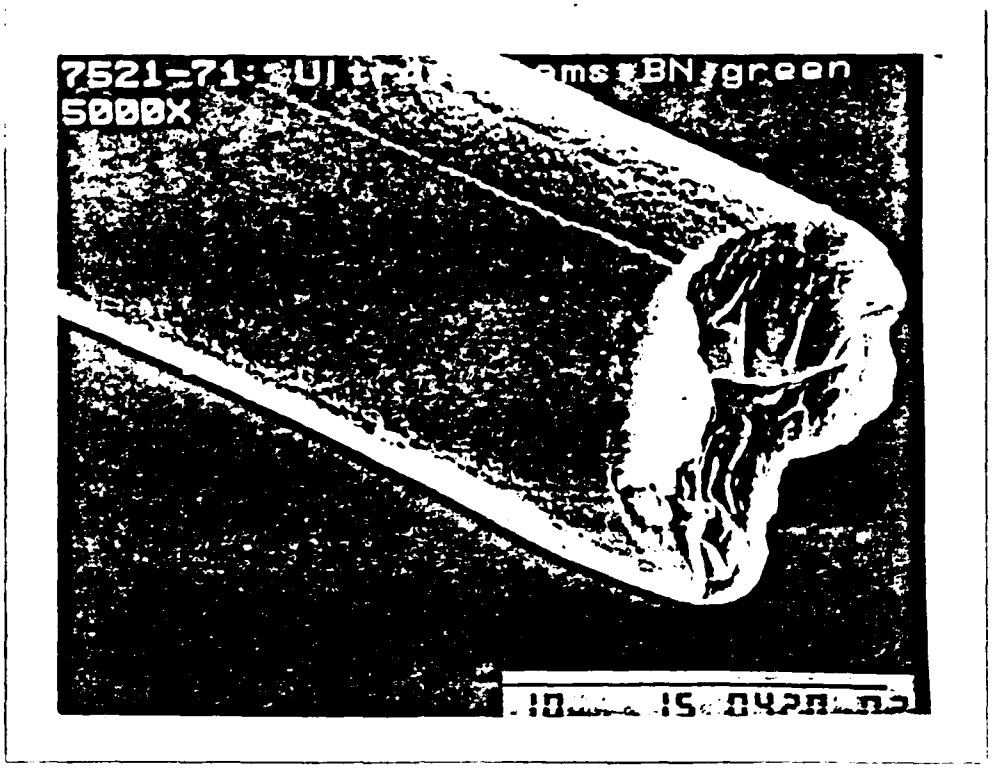

Fig. 3a CROSS-SECTION OF BN PRECURSOR FIBER

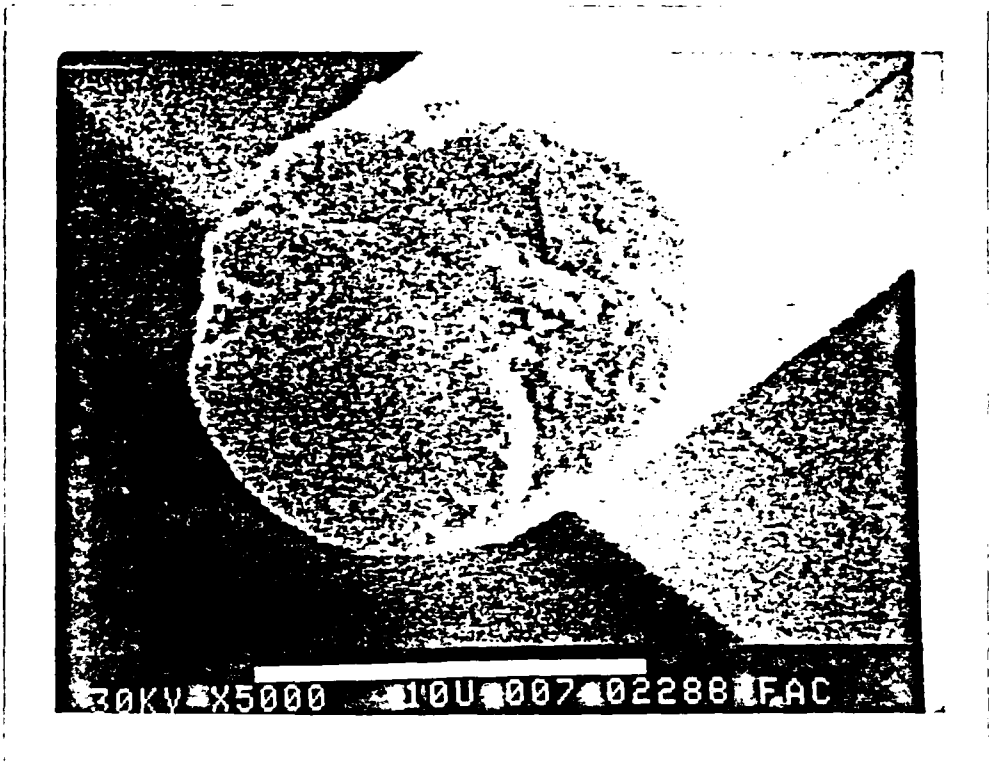

Fig. 3b CROSS-SECTION OF CURED BN FIBER

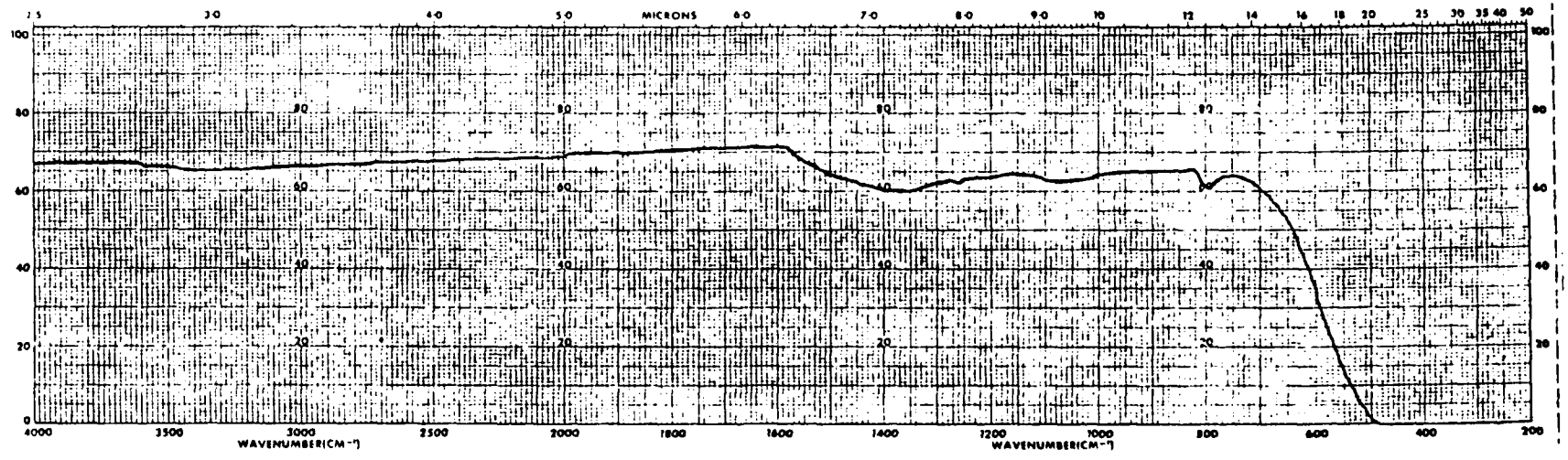

Figure 4

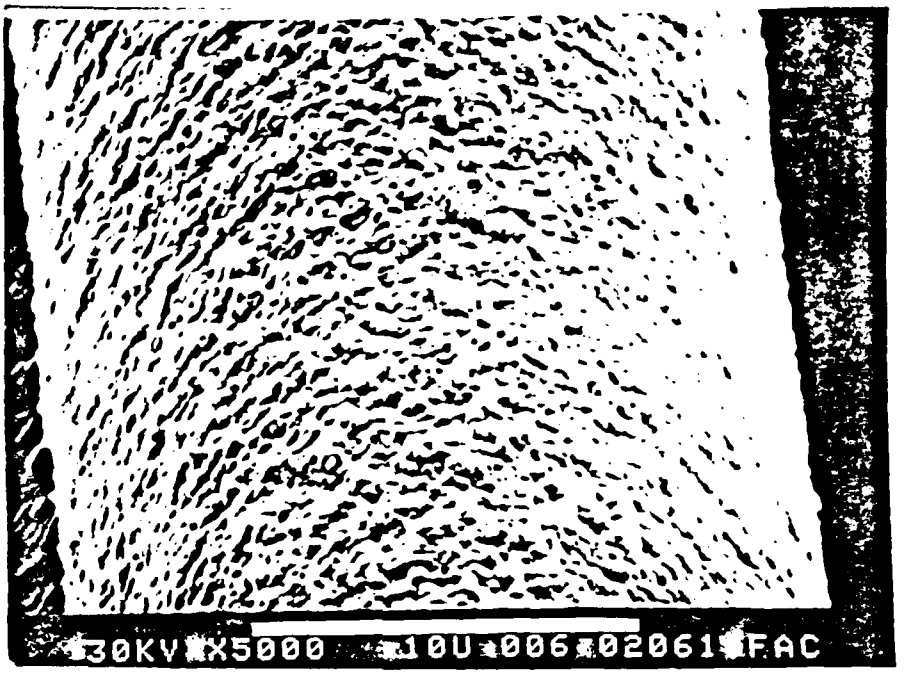

Fig. 5a UNCOATED ALUMINA FP FIBER 5,000x

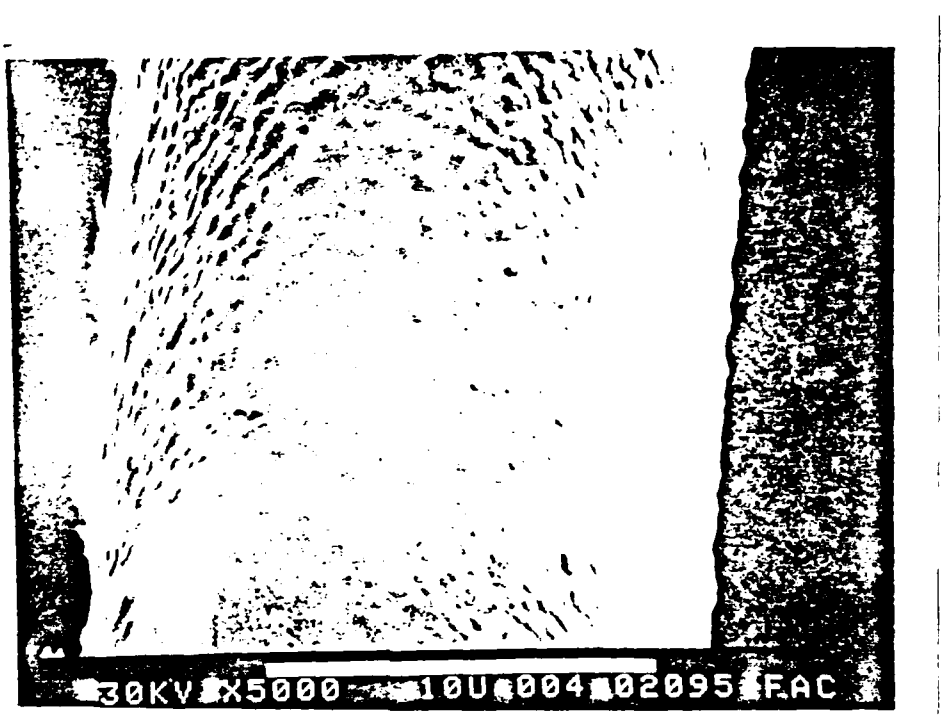

Fig. 5b BN COATED ALUMINA FP FIBER 5,000x

Fig. 6a UNCOATED ALUMINA FP FIBER 10,000x

Fig. 6b BN COATED ALUMINA FP FIBER 10,000x

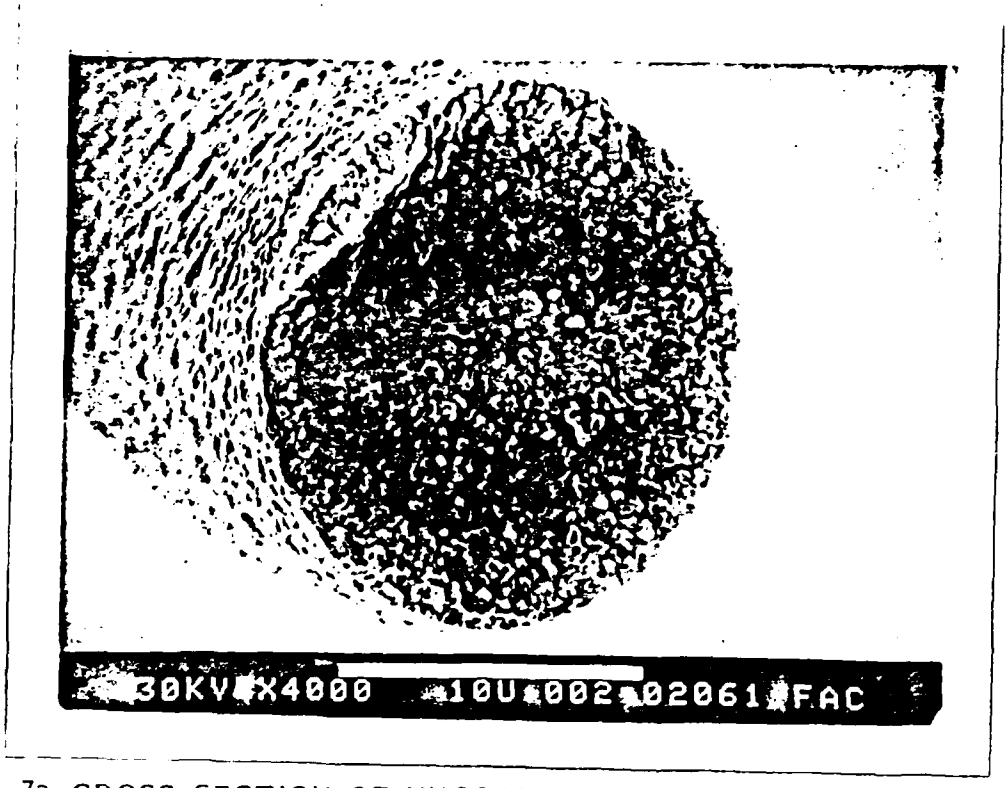

Fig. 7a CROSS-SECTION OF UNCOATED ALUMINA FP FIBER

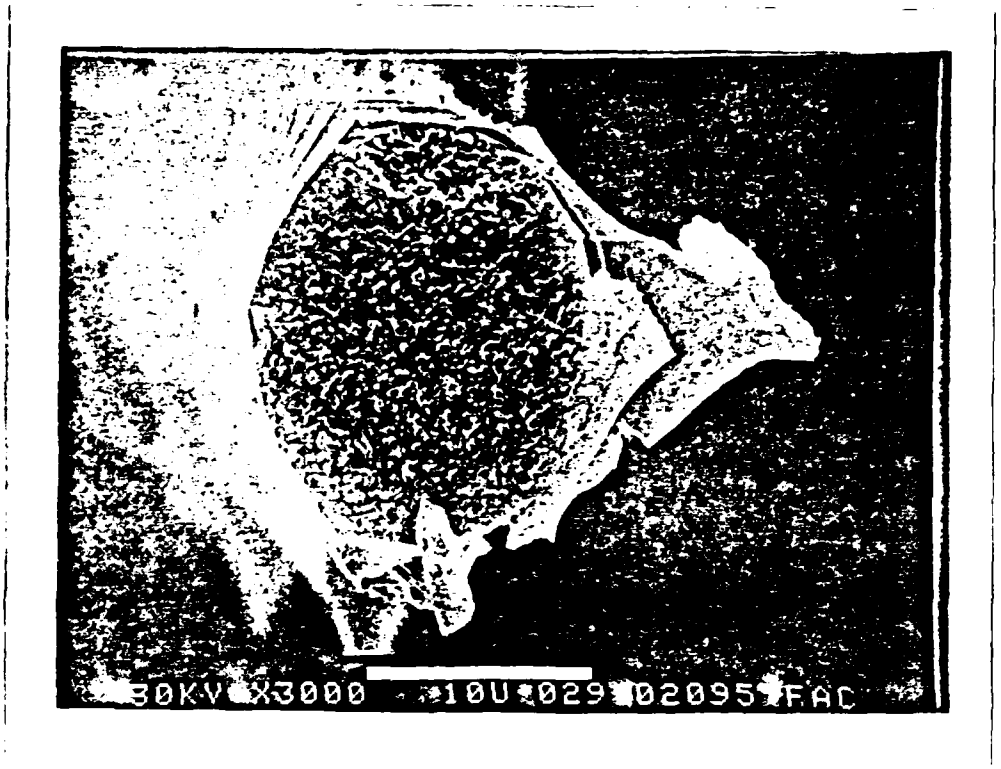

Fig. 7b CROSS-SECTION OF BN COATED ALUMINA FP FIBER